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\begin{document}

\title{Pulse-induced non-equilibrium dynamics of acetylene inside carbon
nanotube studied by an ab initio approach}

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\begin{abstract}
Nanoscale molecular confinement substantially modifies the functionality
and electronic properties of encapsulated molecules.
Many works have approached this problem from the perspective of
quantifying ground-state molecular changes, but little is known about
the non-equilibrium dynamics of encapsulated molecular system. In this
letter, we report an analysis of the non-equilibrium dynamics of
acetylene ( $C_2H_2$ ) inside a semiconducting carbon nanotube (CNT).
An ultrashort high-intense laser pulse (2 fs width and  $10^{15}$  W/cm2
intensity) brings the systems out of equilibrium. This process is modeled
by comprehensive first-principles time-dependent density functional
simulations.
When encapsulated, acetylene dimer, unlike a single acetylene molecule,
exhibits correlated vibrational dynamics (C-C bond rotation and H-C-C
bending) that is markedly different from the dynamics observed in the gas
phase.
This result highlights the role of CNT in modulating the optical electric
field within the tube. At longer simulation time scales ( $>20$  fs) in the
largest-diameter tube studied here (CNT(14,0)), we observe synchronized
rotation about the C-C axes in the dimer and ultimately ejection of one
of the four hydrogen atoms. Our results illustrate the richness of
photochemical phenomena in confined geometries.
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\end{abstract}

\keywords{carbon nanotube | femtosecond laser | time-dependent density functional theory }

\maketitle

Since the first report on the possibility of various chiral structures of carbon nanotubes (CNTs)~\cite{Iijima1991} and the subsequent realization of chiral CNTs~\cite{Iijima1993}, considerable attention has been paid to the basic science and practical application of CNTs~\cite{AvourisText}. After the discovery of capillary-induced filling of CNT~\cite{Ajayan}, molecular encapsulation by CNT has been studied by optical spectroscopy~\cite{Yanagi}. In previous theoretical work, we have found strong electric-field enhancement within a CNT~\cite{ZhangMiyamoto2009} and investigated how such enhancement affects the mechanism of laser-pulse-induced dissociation of encapsulated HCl~\cite{MiyamotoZhangRubio2010} where only hydrogen (H) atoms are expelled with high kinetic energy.

The use of laser pulses has been theoretically explored for eliminating Stone-Wales defects in CNT with a pulse width of 50 fs~\cite{PulseStoneWalse}. The reverse process of creating this defect with a laser is a rare event requiring localization induced by the lattice vibrations. As will become clear below, the presence of defects in the tube walls would not modify the main conclusions of our present work, that an ultrashort pulse of around 2 fs, promotes electrons to antibonding states of the encapsulated molecules leading in most cases to bond breaking.

This corresponds to a clear case of photoexcitation dynamics in a nanospace, which for hydrocarbons encapsulated in CNT leads to selective ejection of an H atom upon irradiation with an ultrashort laser pulse. Here, we look at the analogous case of the photoexcitation dynamics in a hydrocarbon and investigate whether irradiation with an ultrashort high-intensity laser pulse leads to selective ejection of an H atom.

Acetylene ( $\text{C}_2\text{H}_2$ ) is among the hydrogen-containing molecules that are attracting attention as a potential fuel source. Intermolecular reactions involving the  $\text{C}\equiv\text{C}$  bond of acetylene are expected to be enhanced within nanospaces such as the interior of a CNT. Thus, encapsulation and condensation of acetylene molecules inside CNT has been widely investigated. For example, Kim *et al.*~\cite{Kim2005} proposed a method for storing acetylene molecules and converting them into polyacetylene (PA) by using CNT as a nanosized chemical reactor. Their simulations showed that the process of encapsulating a single acetylene molecule in CNT is exothermic, producing a static capillary force of a fraction of a nano Newton. This force compresses the encapsulated molecules, introducing an effective local pressure of hundreds of mega Pascals inside the CNT~\cite{Macintosh2003}. As a result of this process, a straight, isolated single strand of PA encapsulated inside CNT was found. Their simulation revealed that the orientation and shape stability of the encapsulated PA are dependent on CNT diameter~\cite{C2H2-in-CNT-by-DFT}.

Here, we explore the effect of applying an ultrashort high-intensity laser pulse on the dynamics and reactivity of encapsulated molecules in a CNT. The exothermic nature of encapsulating acetylene in CNT~\cite{Kim2005,Macintosh2003} has previously been confirmed. Our dynamical non-equilibrium study starts by applying a strong 2~fs laser pulse with a wavelength of 800 nm and a maximum electric field ( $E_{\rm max}$ ) of  $10 \sim 12$  V/Å (corresponding to laser power between  $I = 1.327 \sim 1.911 \times 10^{15}$  W/cm<sup>2</sup>) according to  $I = \frac{1}{2} \epsilon_0 c E^2$  where  $\epsilon_0$  is the vacuum permittivity and  $c$  is the speed of light). The polarization of the applied field is kept perpendicular to the tube axis. The applied time-dependent electric field and its polarization are shown in Fig. \ref{Fig1}. Through first-principles time-dependent density functional simulations, we monitor and analyze the dynamics of acetylene molecules inside (14,0) semiconducting CNT. In (14,0) CNT, acetylene can form dimers, whereas it remains as individual molecules in (8,0) CNT. Furthermore, we find correlated vibrational dynamics of acetylene molecules inside (14,0) CNT; the vibration was induced by the ultrashort intense laser pulse and the electric field modulation in a CNT. The dynamics at longer times (for irradiation with  $E_{\rm max} = 10 \sim 12$  V/Å) show clear evidence of molecular rotations. For higher intensities,  $E_{\rm max} = 12$  V/Å, we find that one of the acetylenes in the dimer releases a high-kinetic-energy H atom. In what follows, the findings from our comprehensive excited-state simulations are described in detail.

## \section{Stable structure of acetylene encapsulated in CNT}

First of all, we revisit the ground-state configuration of acetylene encapsulated in CNT. Our results are consistent with those reported by Canto et al.~\cite{C2H2-in-CNT-by-DFT}, who studied the interaction between encapsulated acetylene and armchair CNT. Using the local density approximation~\cite{PZ} (LDA) as implemented in VASP code~\cite{VASP1996,VASP1996-2,VASP1999}, we compute the binding energy (BE) of acetylene inside different semiconducting CNTs. The BE per encapsulated acetylene molecule is defined as

$$BE = \frac{1}{n} [E_{\rm total}(\text{CNT}) + nE_{\rm total}(\text{C}_2\text{H}_2) - E_{\rm total}(\text{CNT} + n\text{C}_2\text{H}_2)]$$

where  $E_{\rm total}(\text{CNT})$  and  $E_{\rm total}(\text{C}_2\text{H}_2)$  denote the total energy of isolated CNT and acetylene, respectively, and  $E_{\rm total}(\text{CNT} + n\text{C}_2\text{H}_2)$  denotes that of  $n$  acetylene molecules encapsulated in CNT.

For a single acetylene inside (8,0) CNT or (14,0) CNT, the respective BE is 0.30 eV~\cite{bind80} or 0.03 eV for acetylene parallel to the tube axis.

In (8,0) CNT, binding does not occur between two acetylenes, indicating that the tube diameter is too small to accommodate the acetylene dimer. In contrast, in the larger (14,0) CNT, the BE for single acetylene molecule is smaller and in the similar order to the BE on planar graphene according to the present investigation. However, in (14,0) CNT, formation of molecular dimer is preferred although the dimerization is not preferred in the gas phase from present calculations. Figure \ref{two-C2H2} shows the typical geometry of the binding configurations. The BE of

0.10 eV per molecule (Fig. \ref{two-C2H2} (a)) corresponds to the configuration where the two acetylenes lie in a plane whose normal is nearly parallel to the tube axis\cite{acetylene-orient}. The increase of BE per molecule manifested preferable formation of acetylene dimer in (14,0) CNT. %According to our energy comparison between addition of single molecule and double molecules of acetylene to (14,0) CNT, preferable formation of acetylene dimer in (14,0) CNT is manifested.

We now focus our attention on (14,0) CNT, in which the acetylenes can be aligned in a plane whose normal is nearly parallel to the tube axis (see side view in Fig. \ref{two-C2H2} (a)). The intermolecular distance is  $\sim 3\text{\AA}$ , which is hard to achieve in the gas phase. Such a short intermolecular distance gives rise to the emergence of photo-excited dynamical intermolecular correlations.

## \section{Dynamics induced by femtosecond laser pulse}

### \subsection{Comparative study of acetylene dynamics in different environments}

We now analyze in depth the dynamics triggered by the ultrashort pulse shown in Fig. \ref{Fig1} ( $E_{\text{max}}=12\text{ V/\AA}$ ) on a single acetylene molecule and an acetylene dimer, either free-standing or encapsulated in (14,0) CNT. We have applied molecular dynamics (MD) simulation coupled with electron dynamics within the time-dependent density functional theory (TDDFT). In the relaxed configuration, the C--C axis is not exactly perpendicular to tube axis, and thus each acetylene molecule in the dimer starts to rotate its C--C axis when an optical electric field is applied with polarization exactly perpendicular to the tube axis. Figure \ref{Fig\_comparison} shows the difference in dynamics on a 20 fs time scale. Note that the configuration of the acetylene dimer shown here is the same as in Fig. \ref{two-C2H2} (a) without the CNT. Comparing the three cases allows us to consider the effect of intermolecular interference and nanospace confinement on laser-induced dynamics. In the calculations, the single acetylene molecule simply expels H atoms along the direction of the original C--H bonds. Meanwhile, the acetylene dimer exhibits C--C--H bending without any indication of H emission within 20 fs. Interestingly, the C--C--H bending goes in opposite directions when the acetylene dimer is encapsulated in (14,0) CNT and when it is free-standing. Therefore, the tube wall serves to modulate the applied optical electric field. We note that the tube diameter expands throughout the simulation.

### \subsection{Long-time simulations of acetylene dynamics inside CNT}

The results of the TDDFT-MD simulation on a longer time scale for the acetylene dimer in (14,0) CNT are shown in Figure \ref{Fig\_tb140-2C2H2}. The acetylenes in the dimer have synchronized dynamics; in both acetylenes for the two laser intensities studied here, the time evolution of C--C length, as well as of C--C polar angle (i.e., the angle of rotation about the axis perpendicular to the CNT axis), was the same. However, for the higher laser intensity ( $E_{\text{max}}=12\text{ V/\AA}$ ), the acetylenes' C--C polar angles start to differ at 90 fs. We note that the calculated rotation time is much faster than the typical rotation of acetylene at thermal equilibrium. Here, the polar angles of the two acetylenes rotate almost 45 degrees within 90 fs, that corresponds to approximately 720 fs for one revolution, whereas rotation takes over 1 ps at thermal equilibrium. Such high rotation speed is

linked to the non-equilibrium dynamics induced by irradiation with an ultrashort high-intensity laser pulse.

Although the vibrational dynamics of the C--C bond are synchronized, no correlation is observed in the H atom dynamics. When  $E_{\text{max}} = 12 \text{ V/\AA}$ , there is rapid bending (change in the C--C--H angle) with period of  $30 \sim 60 \text{ fs}$ , and C--H stretching. The shortest stretching mode has a period of  $20 \text{ fs}$  ( $1667 \text{ cm}^{-1}$ ), which is about half that of the typical C--H stretching mode in acetylene ( $\sim 3000 \text{ cm}^{-1}$ )<sup>\cite{Metzelthin2008}</sup>; the force constants in acetylene are considerably lowered by irradiation with the laser pulse.

The reduction of the C--H bond strength can be intuitively understood by the antibonding character of the C--H bond, which is evident in the variation of the charge density monitored throughout the MD simulation. Figure \ref{contour} shows a snapshot at  $t = 50 \text{ fs}$  with  $E_{\text{max}} = 12 \text{ V/\AA}$ . The contour lines of charge redistribution displayed in Fig. \ref{contour} were obtained by subtracting the charge density of the electronic ground state from the time-dependent charge obtained through the present simulation with common atomic coordinates. The cross section of the contour lines corresponds to a plane parallel to one of the two acetylene molecules, which will release a hydrogen atom later. The accumulation and depletion of electrons (denoted as 'electrons' and 'holes') demonstrate how the upper C-H bond weakens due to the important charge redistribution (clear from the density of the contour lines in Fig. \ref{contour}). Finally, as a result of the synchronized dynamics, one of the four H atoms is ejected at  $90 \text{ fs}$ .

% after one full-cycle of CNT expansion and shrink.

This result might be relevant for understanding and examining the generation of hydrogen fuel from hydrogen-containing molecules inside CNTs.

%(CHECK THIS AND ADD MORE DISCUSSION IF NEEDED)

An important question to address is whether the (14,0) CNT is able to withstand such a strong pulse. To answer this, we monitor the change in CNT diameter as a function of time to see whether the diameter expands or oscillates. Figure \ref{Rate} shows the radial dynamics of (14,0) CNT in the current simulation averaged in the whole radial directions.

For a laser intensity of  $E_{\text{max}} = 12 \text{ V/\AA}$ , the expansion rate of the tube diameter tends to approach a finite value, whereas for  $E_{\text{max}} = 10 \text{ V/\AA}$  the rate decreases rapidly and appears to become zero at  $140 \text{ fs}$  and increases again at  $150 \text{ fs}$ . In more detail, the CNT expansion rate remains positive in the E-field direction while negative in the E-field normal direction at  $150 \text{ fs}$ .

As this anisotropic motion has a longer period than the breathing mode of the (14,0) CNT we tentatively conclude that the carbon nanotube threshold is around  $E_{\text{max}} = 10 \text{ V/\AA}$  that is smaller than the threshold for H emission. Note however that for short laser pulses the tube survives higher intensities and the encapsulated molecule inside emitted its H atom<sup>\cite{MiyamotoZhangRubio2010}</sup>.

## \section{Summary and discussion}

Through extensive first principles simulations, we have tested various stable configurations of acetylene molecules encapsulated inside (8,0) and (14,0) semiconducting CNTs. We observed the dimerization of acetylene inside (14,0) CNT but not (8,0) CNT. The comparative study of the dynamics of acetylene molecules irradiated with an ultrashort high-intensity laser pulse suggests the presence of correlated vibration dynamics, that is not found in a single, isolated acetylene molecule and

that differs from the correlated dynamics of an isolated acetylene dimer. The dynamics of a single acetylene resulted in ejection of a high-energy H-atom, and the dimer showed C--C--H bending, both when free-standing and when encapsulated in CNT. The C--C--H bending occurs in opposite directions when the dimer is free-standing and when it is encapsulated in CNT. This difference is interpreted as modulation of the internal electric field by the nanotube wall, as has been studied previously~\cite{ZhangMiyamoto2009}. Finally, a simulation run on a longer time scale revealed synchronized rotation about the C--C axes of the dimer encapsulated in CNT. The direction of rotation was influenced by the laser pulse polarization. In the results discussed here, the rotation occurred along the polar angle. We expect that rotation around an axis parallel to the CNT axis should be observed when the polarization is perpendicular both to the acetylene molecule and to the tube axis. Whether such synchronized rotational dynamics of acetylene molecules enhances the formation of PA is a question of fundamental interest. Although current simulations did not give any evidence of PA formation, the current findings open the door to the development of photochemistry for molecules encapsulated in CNTs, as illustrated here for the case of acetylene.

The change of orientation modifies conductance of CNT and thus this phenomena is important for CNT application to nano-electronics. The current simulation, however, suggests the possibility of molecular rotation control induced by a {\em dynamical}  $E$  field~\cite{StaticE}. We hope that these conclusions will inspire further experimental work employing ultrashort laser pulses in nanomaterials research.

\begin{appendix}

\section{Computational conditions for static calculations}

To determine the electronic ground state, we performed plane-wave density-functional theory total energy minimization calculations~\cite{IZC}. A cutoff energy of 60 Ry was chosen for the plane-wave basis set, and LDA~\cite{PZ} was adopted. Interactions between valence electrons and ions were expressed by using norm-conserving soft pseudopotentials~\cite{TM}. Periodic boundary conditions for both (8,0) and (14,0) CNTs were employed in which inter-tube distance (wall-to-wall distance) was kept as 10  $\text{\AA}$  in order to avoid artificial inter-tube interactions. Along with tube axis, twice of the original period was used. Two irreducible  $k$ -points along the tube axis were considered for the phase-space Brillouin-zone integration.

\section{Choice of exchange-correlation functional}

We checked the BEs using the generalized gradient approximation (GGA) with the Perdew--Burke--Ernzerhof (PBE) functional~\cite{PBE1996} and found that PBE gives extremely small BEs. No binding in calculation using GGA is also reported between noble gas atom and metal~\cite{Rohlfing2008}. Inclusion of van der Waals interaction can explain the preference of the molecule to align perpendicular to the tube axis~\cite{Tran-Duc2011}, a result that is consistent with experimental results for stacked molecules inside CNT~\cite{Okazaki2011}. We found that the preferable orientation of the acetylene molecule can be explained by using the Lennard-Jones potential~\cite{LJ-test}. The LDA has shortcoming in determining the precise orientation of acetylene inside CNT, yet the LDA functional gives qualitatively reliable results for the purposes of the present work examining feasibility of molecular encapsulation inside CNT. However, we should note that LDA will tend to overestimate the absolute values of BEs. LDA was also shown to give

qualitatively good results for the interaction between CNTs and molecular and atomic hydrogen~\cite{AngelHydrogen}. To improve the BE, we could use more advanced exchange correlation functionals based on exact exchange and the random phase approximation for the correlation part~\cite{Marini2006,Garcia-Gonzalez2007,Kresse2009,Kresse2010,Kresse2011}; however, doing so is not straightforward to implement for real-time propagation in TDDFT calculations.

\section{Computation of laser induced dynamics}

We have employed TDDFT to compute the time evolution of electron wave functions, and to perform molecular dynamics (MD) calculations using the FPSEID code\cite{SuginoMiyamoto}. The Suzuki--Trotter split operator technique\cite{Suzuki1992,Suzuki1993} was used for the real-time propagation of the Kohn--Sham wave functions.

%% addition

Since current approach assumes classical dynamics of ions, forces under electronic excitation need approximated treatment, which is still under progress.

%% addition end

MD calculations were performed using the Hellmann-Feynman forces and Ehrenfest dynamics\cite{Ehrenfest}, leading to MD trajectories running on an average of many mean-field potential energy surfaces.

This approximation is valid for few hundreds of femtoseconds for condensed matter systems where many potential energy surfaces exist. Otherwise, the MD simulation faces the conical intersection where quantum electron-ion correlations, that are not captured by Ehrenfest approach, needs to be considered; note many works are sited in the textbook\cite{Springer2012}.

The applied laser was mimicked by a time-varying electric field expressed, in the Coulomb gauge by time-dependent scalar potential  $V_{\text{ext}}(\mathbf{r}, t)$  (we neglect the small magnetic contributions from the external electromagnetic field)~\cite{AngelE-field}. We then solve the time-dependent Kohn--Sham equations:

$$\begin{aligned} & i\hbar \frac{d}{dt} \psi_n(\mathbf{r}, t) = \left[ H_{\text{KS}}(\mathbf{r}, t) + V_{\text{ext}}(\mathbf{r}, t) \right] \psi_n(\mathbf{r}, t), \\ & \text{\label{TDKSE}} \end{aligned}$$

where  $H_{\text{KS}}(\mathbf{r}, t)$  represents the Kohn--Sham Hamiltonian as a functional of the time-varying charge density  $\rho(\mathbf{r}, t)$ ~\cite{RG}, and  $\psi_n(\mathbf{r}, t)$  represents the time-dependent  $n$ -th Kohn--Sham orbitals.

Again the periodic boundary conditions for both (8,0) and (14,0) CNTs were employed as in the case of static calculations, but the wall-to-wall distance was kept as 10 Å and 20 Å in normal and parallel directions to the electric field. To prevent artificial inter-tube interactions in the direction parallel to the optical field, the periodic boundary condition was taken as twice the wall-to-wall distance in the normal direction. To maintain periodicity of the optical field, it was expressed by a saw-tooth potential that gives spatial periodicity in  $V_{\text{ext}}(\mathbf{r}, t)$  in eq. (\ref{TDKSE}) having rapid polarity change in the middle of the vacuum region.

Throughout the MD simulation, the conservation of energy was confirmed\cite{MiyamotoZhang2008}.

\end{appendix}

\begin{acknowledgments}

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The configuration where the plane normal is perpendicular to tube axis also gives a similar BE but we concluded that the numerical difference in energy is not meaningful under our current computational conditions within LDA, see Fig. \ref{two-C2H2} (b).

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Optimization of central position and orientation of single acetylene molecule inside (14,0) CNT was performed by using Lennard-Jones (LJ) potential, taking interactions between atoms of an acetylene molecule and those on the CNT wall into account. The acetylene structure and CNT structure were assumed to be rigid. The preferred orientation of an acetylene molecule was found to depend on the parameter set for describing C--C and C--H interactions with minimum lengths of the LJ potential. %For example, the perpendicular orientation to CNT axis is preferred when the potential minimum position for C--C interaction was set as \$4.10 \text{ \AA}\$, while that of C--H interaction was set as \$3.34 \text{ \AA}\$. Meanwhile, the parallel orientation was preferred when we set the

potential minimum position as  $2.904 \text{ \AA}$  for C--C and  $2.453 \text{ \AA}$  for C-H.

We believe that the proper parameter set for the LJ potential can explain our current LDA results for single and dimer acetylene molecules inside (14,0) as well as for benzene inside CNT\cite{Tran-Duc2011}, but detailed parameter fitting is beyond the scope of the present study.

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\begin{figure\*}[h]

\scalebox{1.0}{\includegraphics[width=\columnwidth]{Fig1}}

\caption{Red line denotes the time variation of optical electric field, while the dotted line is its Gaussian envelope. Polarization direction of the field with respect to the tube axis is denoted by an arrow in the optimized geometry of two acetylene molecules inside (14,0) CNT.

\label{Fig1} }

\end{figure\*}

\begin{figure\*}[h]

\scalebox{1.0}{\includegraphics[width=\columnwidth]{two-C2H2}}

\caption{Most stable configuration for two acetylene molecules inside a (14,0) CNT. (a) Top view (along tube axis) and side view (perpendicular to tube axis) of two acetylene molecules with the vector normal to their molecular plane almost parallel to the axis of the (14,0) CNT. (b) Two acetylene molecules with the vector normal to their molecular plane perpendicular to the axis of (14,0) CNT. Black and gray balls are carbon and hydrogen atoms, respectively.

\label{two-C2H2} }

\end{figure\*}

\begin{figure\*}[h]

\scalebox{1.0}{\includegraphics[width=\columnwidth]{Fig\_comparision}}

\caption{Dynamics of (a) a single acetylene molecule (b) an acetylene dimer, and (c) the dimer inside (14,0) CNT upon irradiation with a pulse as displayed in Fig. \ref{Fig1}. All figures are displayed from the same orientation parallel to the tube axis. The direction of polarization of the optical electric field is in the lateral direction of these figures. Hatched small circles are H atoms, and others are C atoms.

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\label{Fig_comparision} }
\end{figure*}

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\begin{figure*}[h]
\scalebox{1.0}{\includegraphics[width=\columnwidth]{C2H2-dynamics-in-
CNT}}
\caption{ Dynamics of the acetylene dimers inside (14,0) CNT for longer
time regime. View is perpendicular to the tube axis, but the positions of
C atoms of the CNT are not displayed in order to highlight the dynamics
of acetylene dimers. H atoms are indicated by hatched small circles.
Upper panel shows dynamics triggered by a pulse with maximum intensity of
the optical electric field ( $E_{\rm max}$ ) as  $10\text{ V/\AA}$ ; lower panel,
 $12\text{ V/\AA}$ . The polar angles of acetylene molecules are denoted by
hatched region in the starting geometry with  $E_{\rm max}=10\text{ V/\AA}$ ,
which shows synchronized time evolution.
\label{Fig_tb140-2C2H2} }
\end{figure*}

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\begin{figure*}[h]
\scalebox{1.0}{\includegraphics[width=\columnwidth]{Charge-dynamics50fs}}
\caption{ Charge redistribution at  $t=50\text{ fs}$  with  $E_{\rm max}=12\text{ V/\AA}$ .
The red thick and blue thin curves denote electrons and holes,
respectively. The contour map is on a plane containing one of the two
acetylene molecules inside (14,0) CNT, which will release a hydrogen atom
at a later time, as shown in Fig. \ref{Fig_tb140-2C2H2}.
\label{contour} }
\end{figure*}

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\begin{figure*}[h]
\scalebox{1.0}{\includegraphics[width=\columnwidth]{exp_rate}}
\caption{ Time evolution of the rate of radius expansion of (14,0) CNT
throughout the current simulation. Black and gray lines are for  $E_{\rm max}=12$ ,
and  $10\text{ V/\AA}$ , respectively.
\label{Rate} }
\end{figure*}

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